

Disinfection

Presented By



Operator Training and Certification Unit

Disinfection

- ◆ The destruction of pathogenic organisms
- ◆ Not to be confused with sterilization, which is the destruction of all organisms
- ◆ Chlorine is the most widely used disinfecting chemical
 - easily obtained & inexpensive
 - leaves a residual that can be measured
 - however, it also forms byproducts which may contribute to increased risk of cancer

Disinfection of water may be defined as the destruction of pathogenic or disease-causing organisms. This should not be confused with the term sterilization, which implies that all living organisms have been destroyed. Waterborne diseases such as typhoid fever, dysentery, infectious hepatitis, cholera and general gastrointestinal disorders, which were relatively common in the past, are now very rare due primarily to disinfection.

Alternate Disinfectants

- Chlorine Dioxide

- produced on site w/sodium chlorite
- used to control taste and odors
- does not form byproducts, TTHMs

- Ozone

- produced on site by passing an electrical voltage through oxygen
- very powerful oxidant
- does not form byproducts, TTHMs
- unstable
- high cost
- lack of residual

A number of chemicals are used in the water supply industry for disinfection purposes. These include chlorine, chlorine dioxide and ozone. However, because of economy and effectiveness, chlorine is by far the most widely used water disinfectant.

CHLORINE

- ◆ Discovered in 1774
- ◆ First identified as an element in 1810
- ◆ Early use in water application was for deodorizing capacity.
- ◆ First use of chlorine as a continuous treatment process was in 1902, at Middlekerl, Belgium.
- ◆ First continuous use of chlorine in the US was in 1908. Sodium hypochlorite was used to disinfect a 40 MGD supply for Jersey City, New Jersey.

Properties of Chlorine

- ♦ Atomic Wt. = 35.5
Molecular. Wt. Cl_2 = 71.0
- ♦ Depending on the temp. and pressure Chlorine can exist as a GAS, LIQUID OR SOLID.
- ♦ Greenish Yellow Gas
- ♦ Packed as liquefied gas in cylinders
- ♦ Not Explosive or Flammable
- ♦ Cl_2 gas is 2.5 times heavier than air
- ♦ Cl_2 liquid is 1.5 times heavier than water
- ♦ Less than 3 ppm in the air can be detected by nose
- ♦ Dry gas is not Corrosive; but is very corrosive in moist environment

Chlorine can exist as a solid, liquid or gas, depending on the temperature and pressure. In its gaseous state, chlorine is greenish-yellow in color and is about 2.5 times as heavy as air. As a liquid, it is amber colored and about 1.5 times as heavy as water. It is only slightly soluble in water with a maximum solubility of about 1% at 49.2°F. At temperatures below this point, it combines with water to form chlorine "ice", a crystalline substance which may cause operational difficulties in gas chlorinators. Chlorine is not explosive or flammable. In its dry form, it is not corrosive. However, in the presence of moisture, chlorine can be very corrosive.

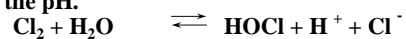
Health Concerns due to Chlorine Gas

- ◆ 3.5 ppm – chlorine odor can be detected
- ◆ 4 ppm – can be inhaled up to 1 hour
- ◆ 15 ppm – produces throat irritation
- ◆ 40-60 ppm – 30 minute exposure is dangerous
- ◆ 1000 ppm – few breaths can be fatal

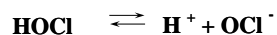
Chlorine gas has a penetrating and irritating odor. In low concentrations, it is an irritant to mucus membranes and the respiratory system. In high concentrations, it can cause death by suffocation. The least amount of chlorine gas detectable by smell is about 3.5 ppm in the air. The maximum amount that can be inhaled for one hour without serious effects is about 4 ppm. At 15 ppm in the air, chlorine will cause irritation of the throat; at 30 ppm it will cause serious coughing spells; and at 40 to 60 ppm, it is extremely dangerous even for a ½ hour exposure. Just a few breaths of air containing 1000 ppm can kill an individual. Liquid chlorine is a skin irritant and can cause damage resembling a burn to body tissues. Because of the above factors, care must be exercised when handling chlorine. Proper ventilation should be provided and appropriate protective clothing worn. In addition, air masks should be readily available when working with chlorine gas.

Chlorine Reactions

Hypochlorous + Hydrochloric Acids formed,
lowering the pH.



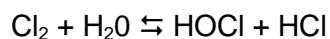
Hypochlorous Acid will further disassociate.



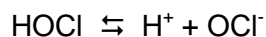
Ammonia Nitrogen compounds in the water
will also react with the Cl_2 , resulting in
“Combined Chlorine”.

Free Avail. Cl_2 + Combined Cl_2 = Total Cl_2

When chlorine is added to water, a mixture of hypochlorous and hydrochloric acids is formed as indicated in the following equation:



Depending on pH, the hypochlorous acid is further reduced to hydrogen and hypochlorite ions as follows:



Chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are all termed free available chlorine.

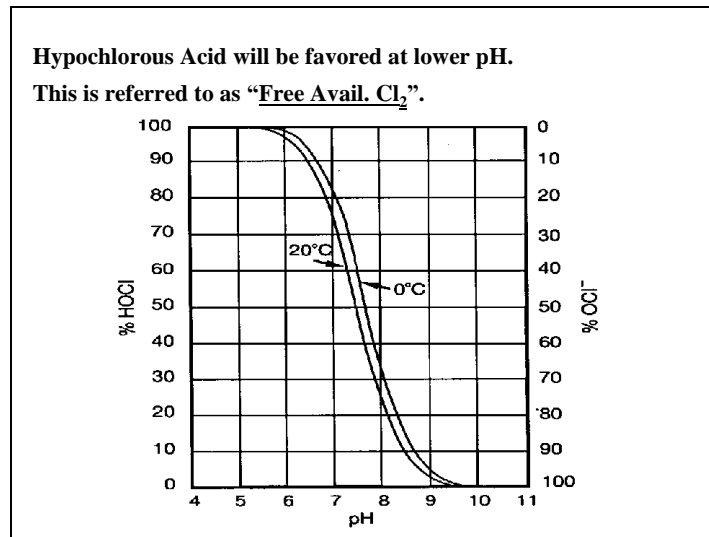


Figure 1

The relative amounts of each are dependent on the pH of the water. As the pH decreases (H increases), more hypochlorous acid (HOCl) will be formed. The effects of pH are illustrated in Figure 1. As can be seen, at the pH values encountered in water treatment, all of the free chlorine will be in the form of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). At a pH of about 7.5, the amount of these two compounds is equal. In terms of oxidation potential though, hypochlorous acid is a much stronger disinfectant than is the hypochlorite ion; about 100 times as powerful. As such, hypochlorous acid is the major disinfectant in most water treatment practices.

Combined Chlorine

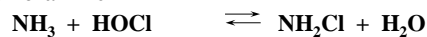
- ◆ Ammonia and/or nitrogen compounds in the water will react with the chlorine resulting in “combined chlorine”

Total residual = combined + free

If nitrogen compounds exist in the water, as is often the case, the hypochlorous acid will react further to form combined chlorine compounds.

Combined Chlorine

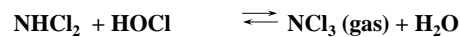
Monochloramine



Dichloramine



Trichloramine

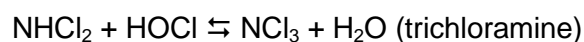
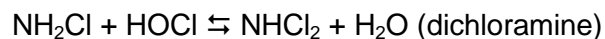
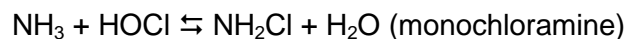


NCl_3 is a gas, has an odor and will escape.

Therefore, an increase in Chlorine dose will result in a drop in Chlorine residual!

Combined Chlorine will decrease as NCl_3 is formed, until eventually Free Chlorine predominates.

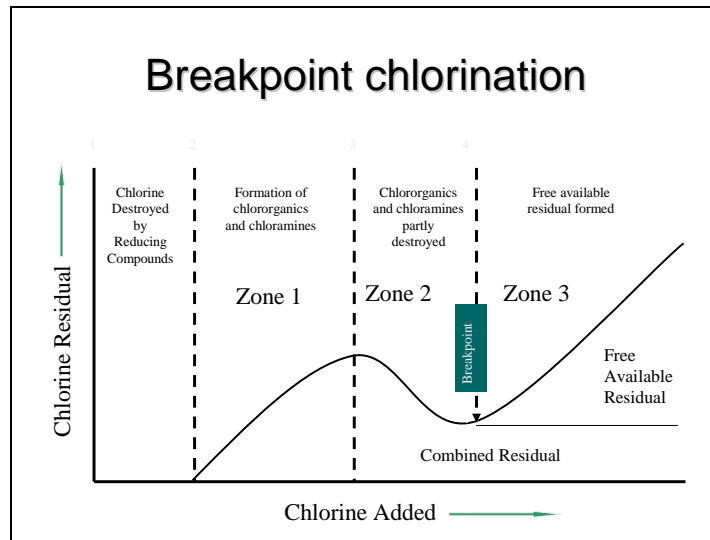
These include monochloramine, dichloramine and trichloramine, and are formed in accordance with the following reactions:



Chloramines

- ◆ Cl_2 + ammonia = chloramines
- ◆ 4 parts Cl_2 to 1 part NH_3
- ◆ About 1/25 powerful as HOCL
- ◆ Used in large distribution systems, more persistent
- ◆ Reduces TTHM formation
- ◆ Attacks biofilms
- ◆ Di and Tri chloramines may cause disagreeable taste and odors

These compounds are weak disinfectants, about 1/25 as powerful as hypochlorous acid. In addition, disagreeable tastes and odors are often associated with combined chlorine.



The shortcomings of combined chlorine (weak disinfectant with associated tastes and odors) can be minimized through the practice of breakpoint chlorination. This practice involves adding enough chlorine to destroy most of the combined chlorine compounds, leaving residual free available chlorine. In zone 1, the predominant chlorine forms are monochloramine and dichloramine. In zone 2, the residual chlorine actually decreases as the monochloramines and dichloramines are converted to trichloramine (nitrogen trichloride), which is released as a gas. The third zone is characterized by a final increase in chlorine residual. Here, an increase in the amount of free available chlorine roughly corresponds to the application of chlorine. The minimum point between the second and third zones is called the breakpoint, and from this point on, any chlorine added should reflect a similar increase in the free residual. In practice, this is known as free residual chlorination, and is by far the preferred method of chlorination. Many waters do not have appreciable amounts of nitrogen present and thus do not exhibit a breakpoint. In this case, free residual chlorination is practiced which implies that sufficient chlorine has been added to produce a predominantly free residual, regardless of whether there is a breakpoint.

Factors Affecting Disinfection with Chlorine

- ◆ pH – the higher the pH, the more hypochlorite ion is present – a much less effective disinfectant
- ◆ Ammonia Nitrogen Compounds – the more ammonia nitrogen compounds that are present the more combined chlorine is formed – a much less effective disinfectant.

So far, we have seen how pH determines the type of free chlorine available (HOCl or OCl^-) and how the presence of ammonia compounds in the water cause the formation of combined chlorine. We have also seen how these two factors, pH and ammonia; can drastically affect the disinfecting power of chlorine. These two factors are reviewed below along with several other factors, which also impact the effectiveness of disinfection.

1. pH - The higher the pH, the more hypochlorous acid (HOCl) is dissociated into hydrogen (H^+) and hypochlorite ion (OCl^-). Although both are free chlorine, hypochlorite ion is a much weaker disinfectant than hypochlorous acid.
2. Ammonia Nitrogen Compounds - The more ammonia nitrogen present in the water, the greater the formation of combined chlorine, which is a weaker disinfectant than free chlorine.

Factors Affecting Disinfection with Chlorine

- ◆ Temperature – higher temperature the faster the rate of reaction (better disinfection). Chlorine is also used up quicker.
- ◆ Time – longer contact time means that better disinfection is more likely.
- ◆ Impurities – the more impurities in the water , the greater the chlorine demand and the less effective disinfection is likely to be.

3. Temperature - The warmer the temperature, the faster the rate of reaction and the quicker disinfection will occur.
4. Time - Chlorine must be in contact with the water long enough for the reaction to occur and to adequately disinfect. The longer the contact time, the more likely the chlorine will have completely reacted.
5. Impurities - Chlorine will react with certain inorganic and organic compounds such as iron and hydrogen sulfide, as well as with bacteria and viruses. A certain amount of chlorine is used up in these reactions and is referred to as chlorine demand. The more impurities in the water, the greater the chlorine demand and the less effective disinfection is likely to be.

Common Chlorine Compounds

◆ Chlorine Gas

- 100% available Chlorine.
- 150 lb Cylinders
- 1 ton Cylinders

◆ Calcium Hypochlorite

- 65% available Chlorine
- Must be Dissolved in Water
- Used in Construction Projects

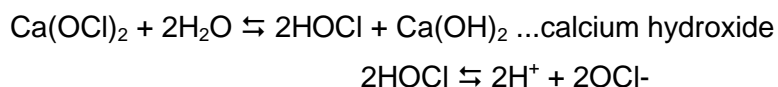
◆ Sodium Hypochlorite

- Liquid (Bleach)
- 3 to 19% (10 -15% typ.) available Chlorine
- Used in Low Volume or Low Rate Applications

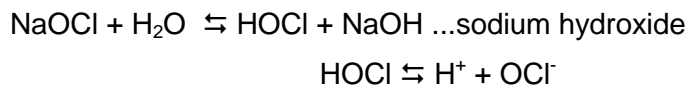
Chlorine Gas (Cl_2) - As a gas, the available chlorine is 100%. This is a liquid chlorine, or gas liquefied under pressure, and is available in 150 pound cylinders and one ton containers. As noted previously, it reacts with water as follows:



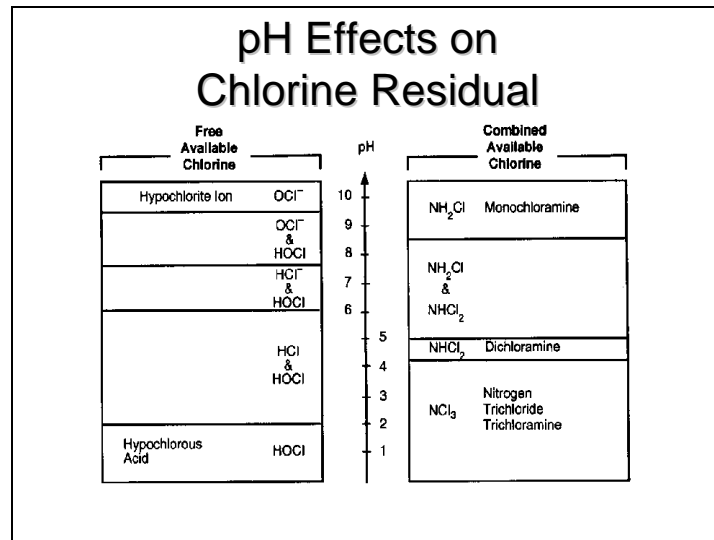
Calcium Hypochlorite ($\text{Ca}[\text{OCl}]_2$) - This is a solid which contains 65% available chlorine. It is produced in powder, granular, and tablet form and is easily shipped and stored. It is sold under various trade names such as "HTH", "Perchloron" and "Pittchlor". This form must either be mixed with water to form a solution and pumped into the system, or added as is to a nonpressurized system. Its reaction with water is as follows:



Sodium Hypochlorite (NaOCl) - This is a liquid containing between 3% and 19% available chlorine. It is sold under numerous trade names such as, "Roman Cleanser", "Clorox Bleach", etc. It can be readily purchased at a variety of locations and is easy to use and handle. Because of this, it is the most common form of chlorine used in small water systems. Its reaction with water is as follows:



All chemicals added to a water supply **MUST** be ANSI/NSF certified



Definitions

- ◆ Available Chlorine:
Refers to the oxidizing power of a chlorine compound.
- ◆ Free Available Chlorine:
The concentration of HOCl and OCl^- ions in the water.
- ◆ Chlorine Applied:
The amount of chlorine added to the water.
- ◆ Total Chlorine Residual:
The amount of chlorine remaining in the free and combined form after a certain contact time.

Available Chlorine: Refers to the oxidizing power of a chlorine compound.

Free Available Chlorine: The concentration of hypochlorous acid and hypochlorite ions in the water.

Chlorine Applied: The amount of chlorine added to the water.

Total Chlorine Residual: The amount of chlorine remaining in the free and combined form after a certain contact time.

Definitions

- ◆ **Free Chlorine Residual:**
The amount of chlorine that has not reacted with other compounds found in the water.
- ◆ **Combined Chlorine Residual:**
The amount of chlorine that has reacted with the natural ammonia or organic nitrogen compounds in the water to form chloramines.
- ◆ **Chlorine Demand:**
The difference between the chlorine applied and the chlorine residual. Usually the amount of the chlorine that has reacted with or is lost to other substances in residual.

Free Chlorine Residual: The amount of chlorine that has not reacted with other compounds found in the water.

Combined Chlorine Residual: The amount of chlorine that has reacted with the natural ammonia or organic nitrogen compounds in the water to form chloramines.

Chlorine Demand: The difference between the chlorine applied and the chlorine residual. Usually the amount of chlorine that has reacted with or is lost to other substances in water and is not found as a free or combined chlorine residual.

$$\text{chlorine applied} - \text{chlorine demand} = \text{chlorine residual}$$

OR

$$\text{Chlorine applied} = \text{chlorine residual} + \text{chlorine demand}$$

Chlorine Applied - Chlorine Demand = Chlorine Residual

Chlorine Residual Measurements

DPD (diethyl-p-phenylene diamine)

◆ **Titrimetric**

- Pink color is removed slowly by adding FAS.
- Chlorine Residual Conc. is calculated by the amount of FAS used to remove all color.

◆ **Colorimetric**

- Relies on color development after DPD is added to the Chlorinated water sample.
- Pink/Red color develops
 - ◆ More chlorine; darker color

In general, practice, it is recommended that enough chlorine be added at the water supply source to maintain a measurable free chlorine residual toward the ends of the water distribution system. To determine the chlorine residual, the DPD (diethyl-p-phenylene diamine) titrimetric and colorimetric methods are used.

The DPD method relies on color development after the addition of the DPD chemical to a sample of chlorinated water. A pinkish color will develop if chlorine is present. The deeper the shade of pink, the more chlorine present. In the colorimetric method, the actual chlorine residual is determined by comparing the color development with known color standards, or by using a spectrophotometer and standard curve. In the titrimetric method, the pink color is removed by slowly adding FAS (ferrous ammonium sulfate) solution. The chlorine residual is then determined by the amount of FAS needed to remove the color.

Most small utilities use the colorimetric method since the equipment is inexpensive, durable and is easily utilized in the field.

Chlorination ByProducts

- ◆ Cl_2 combines with organic matter in water to form:
 - Trihalomethanes (TTHMs)
 - Haloacetic acids (HAA5s)
- ◆ MCL's
 - TTHMs – 80 ppb
 - HAA5s – 60 ppb
- New Rules (Stage 2) require MCL to be met at each location a TTHM/HAA5 sample is collected. This called a Locational Running Annual Average (LRAA)

LRAA = Locational Running Annual Average

STAGE 2 Rules

- ◆ CWS system using chlorine must meet Individual Distribution System Evaluation (IDSE) requirements using one of the following methods
 - Small system waiver
 - 40/30 waiver
 - Standard Monitoring Plan
 - System Specific Study
- ◆ Current sampling continues
- ◆ New sampling begins in 2012 or later based on IDSE results

PPM Formula

- ppm = mg/l when talking about a chemical in water
- $\text{ppm} = \frac{\# \text{ pure chemical}}{\text{M} \# \text{ water}}$
- $\text{ppm} \times \text{M} \# \text{ water} = \# \text{ pure chemical}$
- $\text{ppm} \times \text{M gal water} \times 8.34 \#/\text{gal} = \# \text{ pure chemical}$
- M = one million

CONCENTRATION EXPRESSION

Concentration for chlorine or other elements or compounds in water are commonly expressed in terms of parts per million (ppm) or milligrams per liter (mg/l). Basically, these terms are the same and are interchangeable. A part per million (ppm) can be defined as a part per million parts or as a pound per million pounds. When the term is written as a formula, all the units cancel out and a unitless fraction is left.

When calculating the concentration of a chemical in water, the weight of the chemical is placed on the top of the concentration formula and the weight of water, expressed in millions of units, is put on the bottom of the formula.

Conversion factors

- $\frac{8.34 \text{ \#}}{\text{gallon}}$ or $\frac{\text{gallon}}{8.34 \text{ \#}}$
- $\frac{7.48 \text{ gal}}{\text{ft}^3}$ or $\frac{\text{ft}^3}{7.48 \text{ gal}}$

The two conversion factors discussed above are so important to mathematical computations involving water treatment that they simply must be memorized.

Memorize:

From these two conversion factors, we can develop another important factor:

$$8.34\text{\#/gal} \times 7.48\text{gal/ft}^3 = 62.4 \text{ \#/ft}^3$$

This value is the density of water.